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Effect of pH Values on the Formation and Solubility of Zinc Compounds

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Aqueous suspensions, prepared by mixing the solution of NaOH and that of zinc sulfate, chloride or nitrate, were subjected to aging at 25, 50, and 70°C. Examination of the products by X-ray powder diffraction showed that zinc oxide, basic zinc sulfate, chloride and nitrate are formed depending mainly on the pH. Their solubilities in the suspension media with different pH values were determined at 25°C.

INTRODUCTION

In our laboratory, iron oxides and oxide hydroxides were prepared by wet methods such as the hydrolysis and slow oxidation of aqueous solutions of iron salts. The conditions for the formation of the oxides and oxide hydroxides¹⁾ were reported together with their properties.²⁾ The formation of a variety of products must be considered to be due to the difference in the nature of iron complexes present in the solution just before the formation of a precipitate. It is known that the formation of α -, β -FeO(OH), α -Fe₂O₃ and RFe₃(SO₄)₂(OH)₆ (R=K⁺, Na⁺ or NH₄⁺) takes place by the hydrolysis of iron (III) salts, depending on the pH, kind of an acid anion present, temperature, etc.³⁾ A mechanism of their formation was suggested on the basis of the spectrophotometric and magnetic properties of the iron complexes in the solutions.⁴⁾

It is difficult to make a direct study of the nature in aqueous solutions of the ions of metals such as Zn (II), Pb (II), and W (VI) which have no incomplete *d* electron shell. In order to clarify the mechanism for the formation of the precipitates containing these ions, it was necessary to investigate the conditions for the formation of the precipitates.

When solutions of a zinc salt and NaOH are mixed, a white precipitate is formed. Feitknecht *et al.* reported that the precipitate was transformed into β -Zn(OH)₂ or active ZnO depending on the time lapse of aging.⁵⁾ Basic zinc sulfates and chlorides are formed by the hydrolysis of zinc salts.^{6,7)} A crystalline precipitate of Zn(OH)₂, which has an orthorhombic structure with *a*₀ 8.52, *b*₀ 5.16, and *c*₀ 4.92 Å, can be prepared in the absence of acid anions by the hydrolysis of zinc ions in a solution of NH₄OH⁶⁾ or NaOH.⁸⁾

When white precipitates, prepared by mixing the solution of NaOH and that of ZnCl₂, ZnSO₄, or Zn(NO₃)₂, were subjected to aging at 25, 50, and 70°C, various crystalline precipitates were obtained, depending on the pH, kind of the acid anion and

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temperature. The kinds of precipitates and their solubilities at 25°C and at different pH values of suspension media will be reported.

EXPERIMENTAL

Chemical reagents of an analytical grade were used in the present experiments. Each stock solution containing 1.5 *M* zinc ion was prepared by dissolving the desired quantity of zinc sulfate, chloride or nitrate in conductivity water at room temperature. To 33.3 or 100.0 ml of the acidic solution in a 500 ml cylindrical polyethylene bottle with a narrow inlet neck, the required quantity of 1 *M* NaOH was added in various mol ratios expressed by $2\text{OH}^-/\text{Zn}^{2+}$ ($=R$). Each white suspension in the bottle was diluted with water to 300 ml. The narrow inlet neck of the bottle was closed with a polyethylene stopper and covered with a polyethylene cap. In order to accelerate hydrolysis, the bottles containing the suspensions with $0.01 \leq R \leq 2$ were fixed to a rotating drum in a water bath (50 l) kept at 25, 50, and 70°C, and slowly turned for a period of 20 h or more until the reaction reached equilibrium where no change in pH occurred with a time lapse. After aging, the pH of suspensions was measured using a Horiba-Hitachi electrode pH meter at 25°C. The aging products were separated from the solutions by filtration through filter paper, washed with water and dried at 25°C in a desiccator. All the procedure was carried out in a box under nitrogen atmosphere to prevent carbonation.

The powdery samples obtained in the range $0.1 \leq R \leq 2$ were examined by means of X-ray powder diffraction using $\text{CuK}\alpha$ radiation. The amount of Zn ions in the filtrate was determined by means of EDTA titration.

RESULTS AND DISCUSSION

The pH values of suspensions decrease toward certain values by aging, the difference in pH values before and after aging being comparatively great at $R=1$. The pH values of suspensions with 0.5 *M* ZnSO_4 and ZnCl_2 which have been subjected to aging at 25°C for 100–200 h are plotted against the *R* values in Figs. 1(a) and (b). X-ray analysis indicated that basic zinc sulfates and/or oxide were formed in the presence of sulfates (Fig. 2) depending on the *R* values as shown in Fig. 1(a). In the presence of chlorides, a basic zinc chloride and/or oxide were formed depending on the *R* values as shown in Fig. 1(b). The X-ray diffraction data of the basic chloride was identical with those of $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$.⁹⁾

Suspensions containing 0.15 or 0.5 *M* $\text{Zn}(\text{NO}_3)_2$ were subjected to aging at 25°C for 100–120 h. It was found that a basic zinc nitrate and/or oxide were formed depending on the *R* values. The X-ray diffraction data of the basic zinc nitrate were identical with those of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with a monoclinic crystal structure with a_0 19.18, b_0 6.24, c_0 5.52 Å, and β 93°28'.¹⁰⁾ The pH values after aging are plotted against the *R* values at 0.15 *M* (●) or 0.5 *M* $\text{Zn}(\text{NO}_3)_2$ (○) in Fig. 1(c), together with the aging products. There is no inflection point on the curve in the $R < 1$ range, irrespective of the presence of different products present as a solid phase.

The suspensions were also subjected to aging at 50 and 70°C for 20 h. The basic

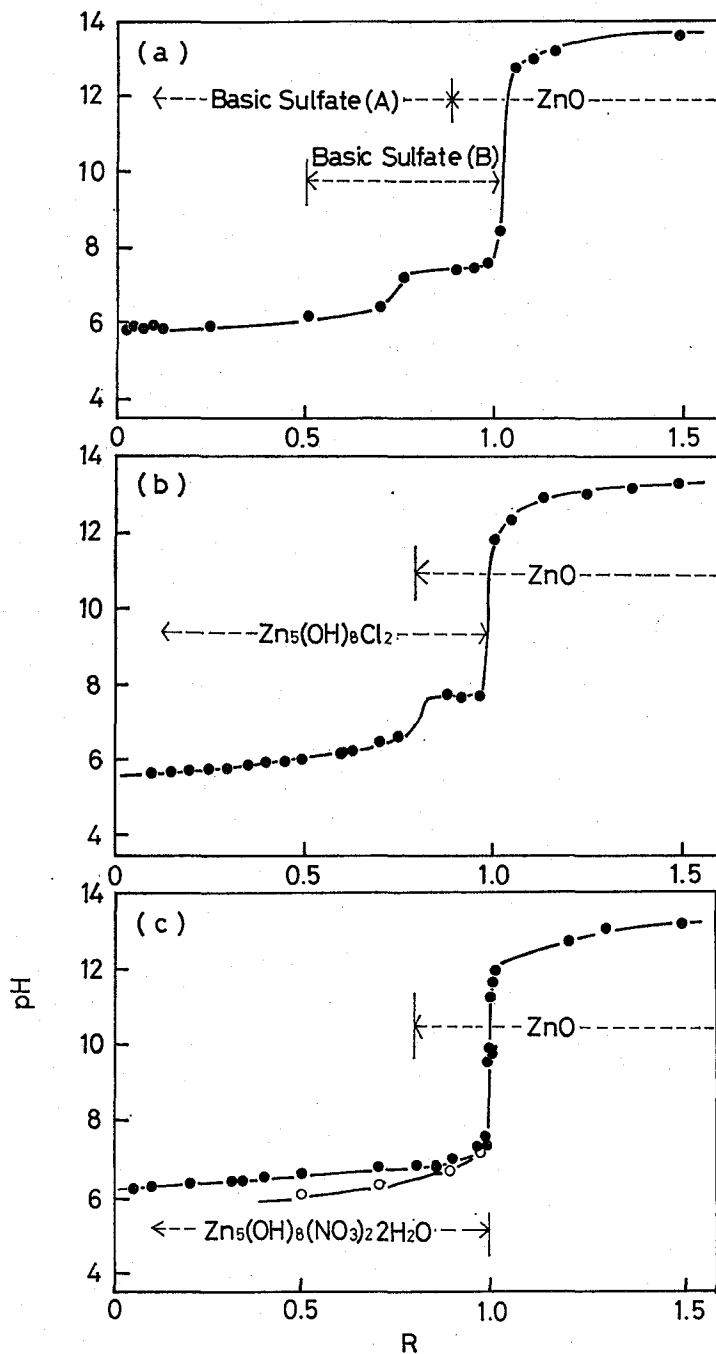


Fig. 1. The pH values after aging at 25°C of suspensions containing 0.5 M ZnSO_4 (a), 0.5 M ZnCl_2 (b) and 0.15 or $0.5\text{ M Zn(NO}_3)_2$ (c).

zinc sulfates, chloride and oxide were obtained in the same R range as above, irrespective of the temperature. In the presence of nitrate, the R range for the formation of the basic zinc nitrate became smaller with the rise in aging temperature. These results

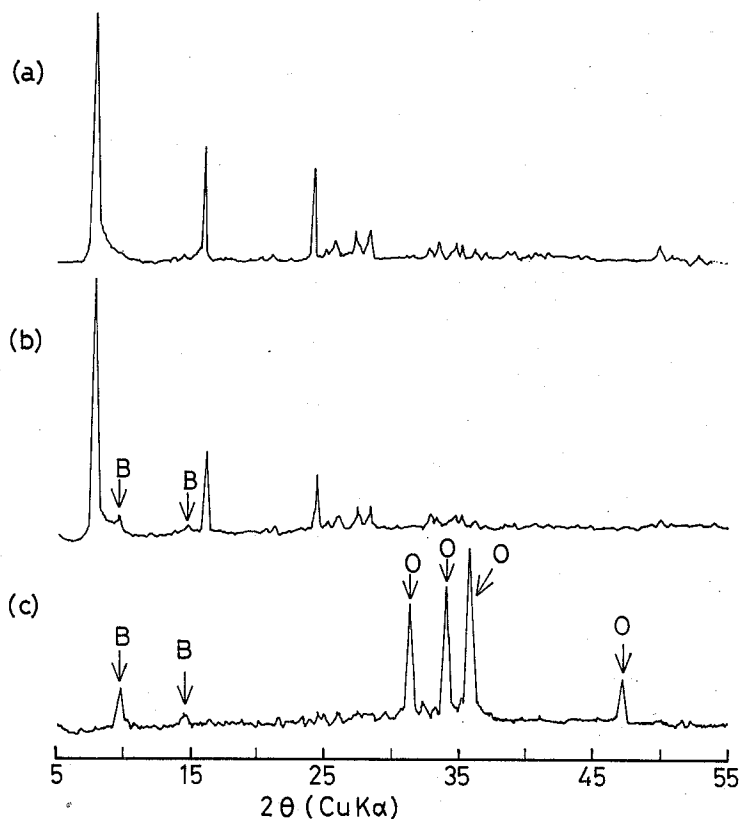


Fig. 2. X-ray diffraction patterns of aging products obtained at $R=0.5$ (a), 0.75 (b), and 1.0 (c), consisting of a basic sulfate A, a mixture of basic sulfates, and a mixture of zinc oxide (indicated by arrow O) and a basic sulfate B (indicated by arrow B), respectively.

indicate that the formation of a crystalline precipitate of $\text{Zn}(\text{OH})_2$ does not proceed in a mixture of aqueous solutions of an alkali and a zinc salt.

The concentrations of zinc ions in the filtrates, obtained by aging at 25°C of the suspensions containing 0.5 M ZnSO_4 , 0.5 M ZnCl_2 or $0.15\text{ M Zn}(\text{NO}_3)_2$, are shown at various pH values of the suspensions in Fig. 3. In the range $\text{pH} < 9$, the points are on straight lines with slopes smaller than 2.0 in spite of the presence of ZnO as a solid phase, whereas in the range $\text{pH} > 11$, the points are on straight lines with slopes -2 . Reichle *et al.* determined the solubilities of $\text{Zn}(\text{OH})_2$ in aqueous suspension media containing either HCl or NaOH at different pH values and at various temperatures.¹¹⁾ Their results determined at 25°C (Fig. 3) show that the points are on lines with slopes smaller than 2.0 for $\text{pH} < 9$ and -2 for $\text{pH} > 11$, irrespective of the presence of $\text{Zn}(\text{OH})_2$. The slopes n indicate that the precipitate of zinc oxide is formed by the hydrolysis of hydroxo complexes containing $[\text{Zn}(\text{OH})_{2-n}]^{2-n}$ or $[\text{Zn}(\text{OH})_4]^{2-}$ ion. The intercepts, which are related to the solubility product, depend on the concentration and kind of the acid anion as a result of the difference in the ionic strength as well known.

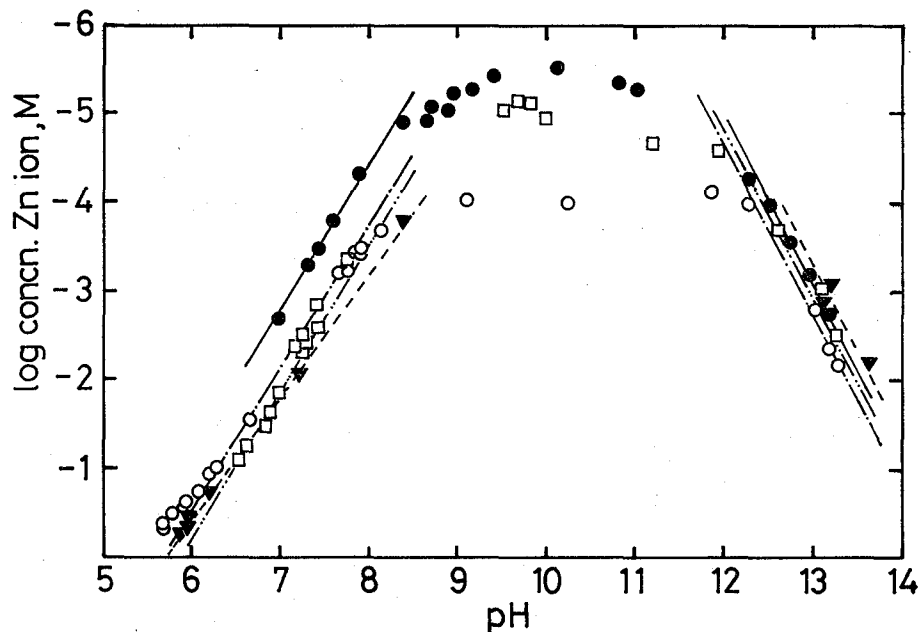


Fig. 3. Solubilities of zinc ions at various pH values in the presence of 0.5 M ZnSO_4 (\blacktriangledown — \blacktriangledown , $n=1.4$ or -2), 0.5 M ZnCl_2 (\bullet — \bigcirc — \bullet , $n=1.6$ or -2) and 0.15 M $\text{Zn}(\text{NO}_3)_2$ (\square — \square , $n=1.6$ or -2). — \bullet — \bullet — obtained by Reichle *et al.* (ref. 11).

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